SUMMARY OF POTENTIAL AMMONIA EMISSIONS FROM NATURAL

SOILS AND CROP FERTILIZER USES

COMMON TO CALIFORNIA

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Introduction and Justification

Ammonia is the dominant gaseous base in the atmosphere and a principal neutralizing agent for atmospheric acids. The supply of alkaline soil dust and gaseous NH_3 available in the atmosphere may control the acidity of precipitation. Volatilized NH_3 may react to form ammonium nitrate or ammonium sulfate and thereby contribute to airborne particulate matter (PM). Nevertheless, NH_3 remains one of the most poorly characterized atmospheric trace compounds. This situation persists as a result of several factors: experimental difficulties associated with NH_3 measurements, rapid gas-to-particle conversion of NH_3 in the atmosphere, capacity of soils, organic matter, and vegetation to act as both sources and sinks for atmospheric NH_3, and variability in nitrogen fertilizer management and related NH_3 emissions (Langford, 1992).

There is a limited amount of published information from which to develop direct emissions estimates of NH_3 for the state of California in general, and the state's Central Valley in particular. Estimated patterns of nitrogen deposition suggest that, for California locations close to photochemical smog source areas, concentrations of oxidized forms of N (NO_2, HNO_3, PAN) dominate, while in areas near agricultural activities the importance of reduced N forms (NH_3 and NH_4^+) may increase significantly (Bytnerowicz and Fenn, 1996). Wintertime concentrations of PM in the San Joaquin Valley have been associated with high levels of ammonium nitrate (Chow et al., 1992). Preliminary measurements of NH_3 background concentrations in the San Joaquin Valley by Fitz et al. (1997) estimated February levels of 3-16 ug m^{-3} around open alfalfa fields.

However, the magnitude and distribution (both regionally and seasonally) of current NH_3 emissions from fertilizer and other agricultural sources is still largely undetermined for the state of California and many other large regions where agriculture is a major land use (Matthews, 1994).

Review of Fertilizer Emission Controllers

The general conditions favoring soil NH_3 emissions from chemical fertilizers have been documented to a limited degree. As a first approximation, high NH_3 volatilization is strongly associated with high soil pH (7-9) levels, although volatilization losses can occur from acid as well as from alkaline soils, due to elevated pH and NH_4^+ concentrations at wet "microsites" where surface-applied urea ($CO[NH_2]_2$) fertilizer particles dissolve and hydrolyze (Fenn and Richards, 1986). Microsite formation of ammonium carbonate ($NH_4^+ HCO_3^-$) by the soil microbial enzyme urease can promote high NH_3 volatilization losses, well after urea is incorporated into the soil organic matter.

Moisture

Soil wetting patterns can strongly influence NH_3 losses. Under certain application conditions, moist soils can emit more of applied fertilizer NH_3 than drier soils (Denmead et al., 1978; McInnes et al., 1986; Burch and Fox, 1989; Al-Kanani, 1991). As already mentioned, hydrolysis of urea is promoted under conditions of elevated soil moisture, which can then enhance evaporation losses as NH_3 and CO_2. Volatilization rates are typically diminished when,

for example, urea can be transported rapidly to deeper soil layers following heavy irrigation

(Fenn and Miyamoto, 1979). Field studies suggest that merely delaying urea application for a

few hours after irrigation to avoid accumulation at wet soil surfaces may be a practical way to

reduce NH_3 volatilization in humid areas (Priebe and Blackmer, 1989). High temperatures and

strong winds may interact with humidity and soil moisture to promote higher volatilization

losses. However, in the winter, natural snow cover and cold temperatures can decrease airborne

soil dust and possibly the evolution of NH_3 from soils (Munger, 1982).

Application Method

Methods of fertilizer application and tillage also have notable impacts on gas losses. As a

general trend, the potential for NH_3 volatilization loss is highest where surface application of

fertilizers is practiced (Fox and Piekielek, 1987), particularly when combined with no-till

management. High rates of band-applied anhydrous ammonia in alkaline soils may retard

nitrification for many days, promoting high NH_3 volatilization rates. Nitrogen oxidizing

reactions may increase as heavy moisture input or mass particle movement subsequently dilutes

the fertilizer-soil microsite reaction zone.

Timing of Application

Understanding the timing of NH_3 volatilization loss from chemical fertilizers is crucial to

accurate field emission measurements. Emission rates measured by Denmead et al. (1982a)

suggest that with anhydrous ammonia injection into a moist clay soil, peak concentrations

occurred about 2 hrs after application and remained elevated at about 25% of peak concentrations

24 hrs later. In other cases, maximum volatilization rates have been reported to occur between

two to six days after fertilizer application (Purakayastha et al., 1997). Typical gas densities

measured for NH_3 in fertilized agricultural systems are on the order of 10-600 ug m^{-3} Denmead

(1983).

Crop Type

To a limited degree, crop attributes have been shown to influence NH_3 volatilization loss

rates. For example, Denmead et al. (1982b) reported that tall (2 m) crops (of corn, in this case)

has lower losses of N during application of anhydrous NH_3 than a shorter (1 m) crop, the

difference attributed to attenuation of wind by the taller crop. Volatilization loss rates of NH_3

from flooded rice fields can be higher than generally measured in unflooded soils (DeDatta et al.,

1991; Bouldin et al., 1991).

Organic Fertilizers

In addition to chemical fertilizer sources, NH_3 volatilization losses from organic

fertilizers can be substantial. Use of liquid manure may result in loss of up to >90% of

ammonium nitrogen from the organic mixture, depending on the intensity of sunlight during field

application (Braschkat et al., 1997). Acidification of slurry can reduce NH_3 emission rates

(Bussink et al., 1994). If organic waste is applied to fields in non-liquid form, irrigation

immediately after spreading may significantly reduce NH_3 emission from the manured plots

(Rodhe et al., 1996). Composting at relatively high temperatures may also reduce NH_3 fluxes

from liquid manure (Brinson et al., 1994).

Loss of NH_3 from stored organic manures and compost has been studied using micro-meteorological mass balance and small wind tunnel experiments, mainly for the purposes of odor control and animal health. It appears that ammonia can be produced from manure via both biological and chemical pathways. Reports indicate that up to about 25% of the total manure nitrogen could be volatilized as NH_3 over a several week period during manure storage, and that changes in pH (>7.5) had the most significant effect on ammonia emissions (Dewes, 1996). Ammonia volatilization from mulches could be negatively correlated with leaf lignin content, whereas green manures seem to emit little NH_3, on either unlimed and limed soils (Glasener and Palm, 1995).

Literature Research and Results

This report on documented NH_3 emission estimates from soils and fertilizers is intended to support subsequent crop field measurements (Krauter et al., in prep.) and computer modeling (Potter and Klooster, 1998; Davidson et al., 1998) for accurate extrapolation of NH_3 emissions from agricultural systems in California's Central Valley and from natural (uncultivated) soils statewide. For this report, we did not attempt to replicate the recent world-wide 'emission factor' reports prepared for the Environmental Protection Agency (EPA), including those by Battye et al. (1994) and MRI (1998). Instead, we report here mainly on the potential range of NH_3 emission estimates for various crop types, fertilizer application methods, and natural vegetation types most common to California.

Because the vast majority of NH_3 emission factors reported in the literature have not been measured in California, these data cannot be used directly for accurate extrapolation to a statewide emission budget for soils and crop fertilizers. Moreover, measured trace gas emission rates from soils are highly variable in space and time, which makes average emission estimates less meaningful and underscores the critical need to characterize local emission conditions for accurate extrapolations in any region. Consequently, the data summarized in this report are intended merely to furnish guidance for new measurements and regional model development on the potential scope of NH_3 emission rates expected in environments similar to those found in California. In this manner, new measurements of NH_3 emissions from fertilizer and soil sources in California can be correctly placed into the larger context of pollution emissions nationwide.

An initial computerized search of the literature uncovered over 80 potential publications and reports from which NH_3 fertilizer emissions might be summarized, compared, and compiled into a useful reference data base for emission ranges. We located approximately 25 citations in the on-line computer listings matching key words for NH_3 emissions and chemical fertilizer management, and more than 60 citations matching key words for NH_3 emissions and organic fertilizer/compost management. In addition, we located several unpublished reports of NH_3 volatilization flux estimates that are accessible on the World-Wide Web (www) sites of numerous agricultural research organizations.

Reported NH_3 emission rates were extracted from these literature and www sources and entered into a spreadsheet data base for a systematic comparison and synthesis of standardized flux ranges, grouped according to natural vegetation types of California (Mayer and Laudenslayer, 1988), predominant crop types in the Central Valley (CDWR, 1993), fertilizer application types, and domestic animals common to California. Crop types follow the land use legend from the California Department of Water Resources system of definitions (CDWR, 1993). To additionally support regional computer modeling for soil NH_3 fluxes (see, for example, Davidson et al., 1998), these crop types have been cross-referenced in a geographic information system (GIS) to STATSGO soil types and seasonal land-cover regions of the United States derived from multi-temporal analysis of satellite images by the U.S. Geological Survey (Loveland et al., 1995).

The comparison of emission estimates for natural soils (Table 1) reveals many missing data values for major natural vegetation types common to California. Only shrub lands and range lands are represented with more than a few published emission measurements. Percentage loss rates may be over 20% of mineralized soil nitrogen, although there is little knowledge of the potential timing and extent of such high NH_3 emissions from natural range lands. No emission information for soil NH_3 is currently available for oak woodland and chaparral ecosystems, which cover a substantial portion of California's wild lands. Information on net NH_3 fluxes in conifer forests of the Sierra Nevada mountain regions is also lacking in the available literature.

We note that, on the basis of the several available measurements reported for natural vegetation types, these maximum flux rates for uncultivated soils are generally 1000 times lower than NH_3 flux rates measured for various crop fertilizer application methods common in California (Table 2). Judging from these data, NH_3 emission rates as a fraction of applied fertilizer N in the forms of urea and organic fertilizer sources appear to be the highest measured so far in agricultural systems, with maximum reported loss rates more than 50% of applied fertilizer N. Maximum loss rates for all other fertilizer types are reported at less than 10% of applied fertilizer N.

Emission factors were categorized also by crop type (Table 3), which again shows the paucity of information available for crop types common in California. Highest percent loss rates have been measured from rice fields, although potential NH_3 emissions appear high in pastures also. No measurement reports for NH_3 emissions were located for common crop types of fruit trees and vineyards in California.

Hence, it is anticipated that the field flux measurements for NH_3 emissions planned now by Krauter et al. in California's Central Valley will be the first of their kind made for crop types of grain, truck, fruit tree, and vineyard in the State, plus new measurements of background NH_3 emissions from nearby natural ecosystems. Tables 1-3 will be continually updated as new NH_3 emission factor measurements in California become available. This tabulated information will be used to calibrate simulation models of soil NH_3 emissions on a statewide basis.

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Table 1. Ammonia Emission Factors for Natural Vegetation Types of California

Code	Vegetation Type	Flux (ug N m-2 hr-1)		Percent Loss		References
		Minimum	Maximum	Minimum	Maximum	
	Tree dominated					
T1f	Needleleaf (mixed)	4.0				Langford & Feshenfeld (1992)
				0.3		Camire and Bernier (1981)
T2a	Broadleaf (oak)					
T2b	Broadleaf (mixed)					
T3	Oak woodland					
T4	Oak savanna					
	Shrub dominated					
S1	Chapparal					
S2	Tall shrubland					
S3	Mixed shrubland					
S4	Low shrubland		5.7			Woodmansee (1978)
S5	Desert shrubland	0.6	114.0			Schlesinger & Peterjohn (1991); West & Skujins
S6	Mixed rangeland	1.3				Schimel et al. (1986)
	Herb dominated					
H1	Shortgrass rangeland	11.4	200.0			Woodmansee (1978); Denmead et al. (1976)
				1.6	23.0	Van der Weerden & Jarvis (1997)
H2	Wet meadow					

Notes:
Single enteries were placed in the minimum column

Table 2.   Ammonia Emission Factors for Fertilizer Types Comnon in California

Code	Fertilizer Type	Flux (ug N m-2 hr-1)		Percent Loss		References
		Minimum	Maximum	Minimum	Maximum	
A	Anhydrous NH3 injected					
				0.9	4.0	Denmead et al. (1977); Bouwman et al (1997)
B	Urea dry					
				4.0	46.0	McInnes et al. (1986); Hargrove et al. (1987)
C	NH4+ compounds dry					
				1.3	3.7	Harding et al. (1963); Kelly & Mengel (1986)
D	UAN liquid					
				2.5		Bouwman et al (1997)
E	Anhydrous NH3 liquid	2760	81000			Denmead et al. (1982b)
				4.0	7.0	Bouwman et al (1997); Denmead et al. (1982b)
F	Organic waste liquid	1980	18000			Vandre and Kaupenjohann (1998)
				14.0	99.0	Braschkat et al. (1997)

Notes:
    Code A is mainly by injection into soil behind a shank or knife to 10-20 cm depth
    Code B is mainly incorporated into soil furrow
    Code C is mainly ammonium nitrate, incorporated into soil furrow
    Code D is urea ammonium nitrate, mainly dripped into irrigation water run
    Code E is mainly dripped into irrigation water run
    Code F is mainly in slurry form added into irrigation water run

Table 3. Ammonia Emission Factors for Crop Types Comnon in California

Code	Crops	Flux (ug N m-2 hr-1)		Percent Loss		References
		Minimum	Maximum	Minimum	Maximum	
G	Grain & Hay					
F	Field & Row	2760	81000	1	7	Denmead et al. (1978); Denmead et al. (1982b)
P	Pasture					
				2.2	43	Kissel et al. (1977); Reynolds & Wolf (1988)
T	Truck & Nursery					
D	Deciduous Tree					
C	Citrus Tree					
V	Vineyard					
R	Rice					
				4	54	Bouldin et al. (1991); DeDatta et al. (1991)

Notes:
    G is a mixture of barley, wheat, and oats
    F is mainly cotton with some corn
    P is mainly alfalfa
    T is mainly tomatoes and melons
    D is mainly almonds and peaches
    C is mainly oranges